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PROPOSED MECHANISMS ON THE FORMATION OF ACIDIC AEROSOLS FROM PRECURSORS

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16. ABSTRACT

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ABSTRACT

Atmospheric particles acidify through the processes of nucleation, condensation, coagulation, and gas-particle chemical reactions. The gas-phase pathway depends on the generation of free radicals that oxidize sulfur dioxide, nitrogen dioxide, and organic compounds to acids, followed by either nucleation or condensation. The aqueous-phase pathway acidification proceeds through the reactions of dissolved reductants and oxidants. The pathways for accumulation of sulfuric acid, nitric acid, and organic acids in particles may differ in responses to factors such as liquid water content of the particles and mass accommodation coefficients of reactants. Laboratory chemical kinetic results indicate that photochemical gas-phase and co-absorbed oxidant reaction pathways for S(IV) may be important simultaneously, for example, in industrial-urban air during the summer. However, during the night and during the winter, aqueous-phase pathways should dominate. Laboratory investigations of the oxidation of nitrogen dioxide indicate that the gas-phase photochemical pathway is important, but the aqueous-phase is not. Gas-phase photochemical oxidation of organics is generally established, but the aqueous-pathways have not received sufficient attention to establish their importance.

INTRODUCTION

The evolution of the atmospheric particle size distribution can be expressed as (Middleton and Brock, 1976; Friedlander, 1977; Gelbard and Seinfeld, 1978):

Rate of Change in Composition/ Size Distribution		Particle Advective Transport			
	=	Particle Convective Transport	+	Growth Rate by Condensation, absorption & Internal Reactions	
	+	Coagulation Rate	+	Primary Particle Input Rate	
	+	Homogeneous Nucleation Rate	+	Removal Rate (e.g., Dry Deposition)	(1)

The processes represented by terms on the right side of Eqn (1) govern the size and chemical distribution of the particles. However, the acidification of particles in the lower troposphere is likely dominated by condensation, absorption, and internal reactions of acids and their precursors. Homogeneous nucleation and coagulation may also be important. The relative contribution of the pathways beginning with either condensation or nucleation will not be considered here. Rather, the chemistry of forming acids from their precursors will be examined.

The chemical pathways for acidifying particles in the lower troposphere are: generation as products of the gas-phase photochemical oxidant cycle; co-absorption and reactions of oxidants and reductants; and metal-ion catalyzed oxidation in aqueous particles (Durham et al., 1982; Calvert, 1983; Calvert and Stockwell, 1984; Martin, 1984; Hoffmann and Jacob, 1984; Schwartz, 1984). Features of the atmospheric aerosol that influence the acidification rate in aqueous particles include the particulate chemical

size distribution and the relative humidity, which determine the liquid water content of the aerosol.

IMPLICATIONS OF PARTICULATE CHEMICAL SIZE DISTRIBUTION

The chemical size distribution of particles commonly found in the polluted lower troposphere has been well established. Except for unusual cases in which primary sources dominate (local industry, marine, fire, etc.), a significant difference is exhibited by particles above and below about 2 μm. The general chemical content is presented in Table I.

TABLE I. GENERAL CHEMICAL CONTENT OF CONTINENTAL PARTICLES IN THE LOWER TROPOSPHERE.*

Diameter < 2 μm "Fine"	Diameter > 2 μm "Coarse"	In Both Fractions	Variable
SO_4^{2-}, C(soot), condensed organic cmpds and acids, NH_4^+, H^+, cmpds of Pb, As, Se	Cmpds of Fe, Ca, Ti, Mg K, Si, Al; organic (pollen, spores)	NO_3^-, Cl^-	Cmpds of Zn, Cu, Sn, Cd, V, Sb

*Adapted from reviews by Durham et al. (1982) and Bradow and Spengler (1982).

Whitby et al. (1972) recognized that the lower tropospheric particulate mass distribution is bimodal, with a minimum at about 2 μm. The fine fraction contains dissolved and solid salts, elemental carbon (soot), organics, and water; it is usually acidic or neutral. The coarse fraction contains mostly insoluble metal oxides and carbonates; it is usually basic. These important observations make several features of atmospheric particle behavior intuitively obvious: (a) the major emission sources of the fine

and coarse fractions are different; (b) a large fraction of the fine fraction is formed from gaseous precursors in the atmosphere; and (c) coagulation is not effective in transferring mass from the fine to the coarse fraction. The NO_3^- and Cl^- observed in the coarse fraction may be due to acidic displacement reactions of HNO_3 and HCl by H_2SO_4 in the fine fraction, followed by sorption by coarse particles. Also, natural sources contribute to the Cl^- content of coarse particles. Thus, from these features, we can expect that the particulate fine fraction may contribute to atmospheric aerosol acidification; except in special cases (oceanic atmospheres), coarse particles do not contribute to a substantial degree.

The ionic content of the fine fraction interacts strongly with atmospheric water vapor (Meszaros, 1971; Winkler and Junge, 1972; Charlson et al., 1978), especially for relative humidities greater than about 30%. Ho et al., (1980) showed that the liquid water content of the fine particles in Los Angeles exceeded 20% of the mass for relative humidity of 60%, and exceeded 50% of the mass for relative humidities greater than 75%. The dissolved ionic content of the fine particles is probably 0.001 to 1 g/l (Stelson and Seinfeld, 1981).

The existence of surface films on fine particles was recognized before 1955 (see review by Durham et al., 1982). The films are probably composed of organics that partition at the air-water interface. The portion of the molecule that is non-polarizable (the "hydrocarbon" chain) orients toward the air, and the portion that is polarizable orients toward the water. These films may affect the water mass transfer rate, which governs evaporation or growth in response to changes in relative humidity. The films may also influence the chemical growth rate (Graedel and Weschler, 1981; Toosi and Novakov, 1985).

Thus, this consistent picture of the particles in the lower troposphere is summarized in Table II.

TABLE II. MODEL FOR POLLUTANT GAS-PARTICLE REACTIONS IN THE LOWER TROPOSPHERE.

Type of Particles	Fine Fraction	Coarse Fraction
Continental	hydrocarbon surface	hydrocarbon surface; solid mineral core
RH < 20%	underlying thin aqueous layer; solid ionic core	
RH > 20%	aqueous core	
Maritime		
RH < 75%	hydrocarbon surface; solid ionic core	hydrocarbon surface; solid ionic core
RH > 75%	hydrocarbon surface; aqueous core	hydrocarbon surface; aqueous core

The chemically active particles are generally ionic solutions that are coated with an organic surfactant. These particles grow and are acidified by condensation (or coagulation) of non-volatile species and the absorption and reaction of oxidants and reductants.

TROPOSPHERIC GAS-PHASE CHEMISTRY

The acidification of particles in the lower troposphere is dependent on oxidant formation (see reviews by Durham et al., 1982 and Durham and Demerjian, 1985). The general photooxidation cycle is illustrated in Fig. 1. Free radicals are generated by photolysis (O_3, HONO, etc.) or dark chemical reactions (O_3 + olefins). These free radicals (HO, RO, HO_2, RO_2) populate the positions shown in Fig. 1 and activate the cycle. RO and HO radicals attack the VOC pool and O_2, producing RO_2 and HO_2, which attack NO to produce NO_2. This principal cycle establishes the O_3-formation cycle.

The oxidizing free radicals react with themselves and pollutants to produce important species for acidifying particles. The most important reactions leading to acid products are:

$$HO + SO_2 \text{ --> } HOSO_2$$
$$+ O_2 + H_2O \text{ --> } HO_2 + H_2SO_4 \quad (2)$$

$$RO_2 + SO_2 \text{ --> --> } H_2SO_4 \quad (3)$$

$$HO + NO_2 \text{ --> } HNO_3 \quad (4)$$

$$RO + NO_2 \text{ --> } RONO_2 \quad (5)$$

$$NO_2 + O_3 \text{ --> } NO_3 + O_2$$
$$NO_3 + NO_2 \text{ --> } N_2O_5$$
$$+ H_2O \text{ --> } 2HNO_3 \quad (6)$$

$$VOC + HO, RO + O_2 \text{ --> } RO_2$$
$$+ NO, NO_2 \text{ --> aldehydes, ketones, alcohols}$$
$$+ \text{free radicals --> carboxylic acids} \quad (7)$$

$$O_2 + O \text{ --> } O_3 \quad (8)$$

$$HO_2 + HO_2 \text{ --> } H_2O_2 \quad (9)$$

Reactions 2-7 form H_2SO_4, HNO_3, and carboxylic acids, which may either condense on existing particles, or nucleate new particles. Reaction 2 also leads to the formation HO_2, which may increase the atmosphere's potential for forming H_2O_2 (Stockwell and Calvert, 1983). The molecular oxidant products H_2O_2 and O_3 are important aqueous phase reactants.

Thus, the important gas-phase reactants for forming acids and precursor oxidants (H_2O_2, O_3) are the oxidizing free radicals (HO, RO, HO_2, RO_2, and O).

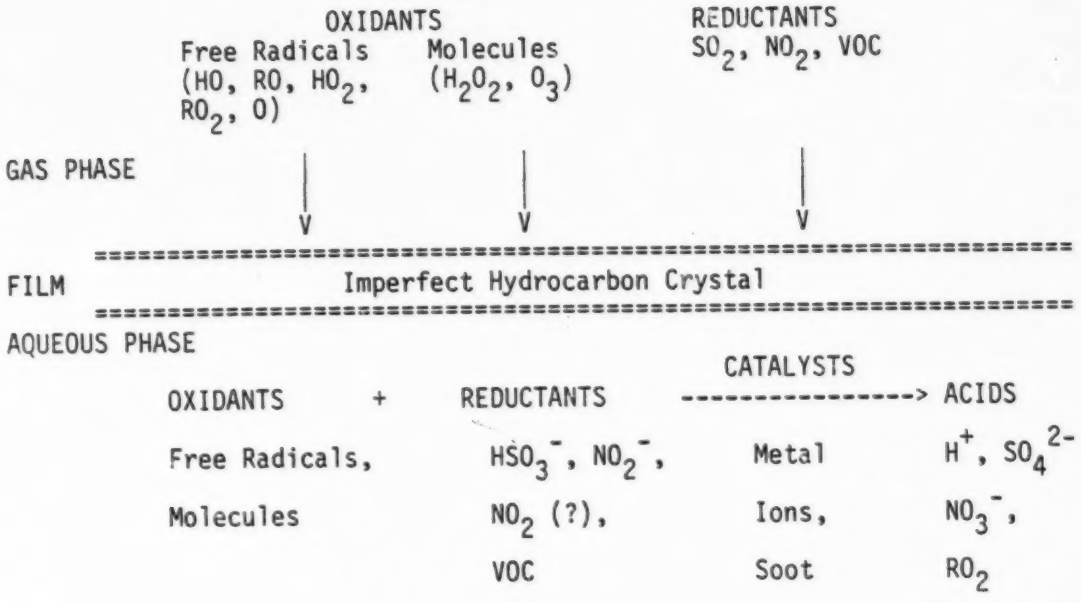

Figure 2. Idealized model of atmospheric particle growth and acidification.

AQUEOUS-PHASE CHEMISTRY: UNCATALYZED

The aqueous-phase acidification may occur through the absorption and reaction of gas-phase oxidants and reductants, or through the absorption of reductants during a period of aqueous-phase oxidant generation. These pathways are shown in Fig. 2. Oxidant and reductant transport effectivenesses through the postulated surfactant film are not known. Two major resistances must be overcome: (a) the adsorption of the gaseous species on the hydrocarbon surface, which is governed by the mass accommodation coefficient α, and (b) diffusion through the surfactant, followed by solvation in the aqueous core. The surfactant may be regarded as a thin, imperfect hydrocarbon crystal that offers little resistance to the diffusive transport of non-reactive species. However, reactive species may be substantially depleted in the surfactant.

The values of α for the reductants and oxidants are not known. The flux of a gaseous species "s" through the surfactant is proportional to $\alpha[s]$. Values commonly observed for α are in the range of 10^{-2} to 10^{-10}. The ratio of fluxes of an oxidant and a reductant is

$$\frac{\text{Flux(OX)}}{\text{Flux(RED)}} = \frac{\alpha(\text{OX})[\text{OX}]}{\alpha(\text{RED})[\text{RED}]} \qquad (10)$$

A reasonable range of α's ratio is 10^{-8} to 10^{8}, which greatly exceeds that for concentration ratios; see Table III for typical values in polluted urban air. Excluding consideration of HO and O, the range of reductant-oxidant concentration ratios is approximately 1 to 10. For aqueous reactions that are rapid, the conversion may be controlled by one of the reactant's value of α.

TABLE III. TYPICAL VALUES OF POLLUTANT CONCENTRATIONS IN URBAN AIR[a]

Species:	SO_2	NO_2	VOC	H_2O_2	O_3	HO_2	HO	O
Concn, ppb:	10	20	10	10	100	0.5	10^{-4}	10^{-5}

a. Adapted from NAS (1977)

Chemical reactions of the surfactant with the free radicals O, HO, and RO are likely of the type (R' is immobile):

$$\text{O} + \text{R'H} \text{ --> } \text{HO} + \text{R'} \qquad (11)$$

$$\text{HO} + \text{R'H} \text{ --> } \text{H}_2\text{O} + \text{R'} \qquad (12)$$

$$\text{or} \quad \text{HOR'H}$$

$$\text{RO} + \text{R'H} \text{ --> } \text{ROH} + \text{R'} \qquad (13)$$

Even if the values of α are high, the surfactant likely depletes these three free radicals before they diffuse to the aqueous core. The reactions may produce cross-linking in the surfactant by R' + R' combinations. However,

adsorbed peroxy radicals do not react with hydrocarbons and should diffuse through the surfactant, producing solvated peroxy:

$$HO_2 + R'H \rightarrow HO_{2(aq)}\cdot + R'H \quad (14)$$

$$RO_2 + R'H \rightarrow RO_{2(aq)} + R'H \quad (15)$$

The mass accommodation coefficients of HO_2 and RO_2 on hydrocarbon surfaces are not known and may be too low for the surfactant film for free radical absorption to be an important oxidation pathway. However, if α for HO_2 is > 40x that for H_2O_2, then HO_2 flux should yield as much $H_2O_{2(aq)}$ as absorbed directly from the gas phase. Calculations by Chameides and Davis (1982) for the absorption of HO and HO_2 by cloud nuclei indicate for $\alpha > 10^{-4}$ that the gas-phase scavenging pathway may be important for providing direct oxidizers or for forming $H_2O_{2(aq)}$. Schwartz (1984) has performed similar calculations for HO_2 and suggests that α should be $>10^{-3}$ for the pathway to be important for acidifying clouds.

O_3 may react with the hydrocarbon chains (Cooper and Prober, 1960) of the surfactant, but its reaction rate constant is small; if O_3 is adsorbed on the surfactant, it likely penetrates with little depletion to the aqueous core. H_2O_2, SO_2, and VOC adsorbed on the surfactant are expected to diffuse through the hydrocarbon chains without reacting with them and dissolve in the aqueous core. NO_2 is insufficiently soluble for its oxidation in the aqueous core to be an important pathway for producing HNO_3; the effectiveness of reactions on or in the surfactant have not been explored.

In the aqueous core, the oxidation-reduction reactions that lead to acidification have been well-investigated for formation of H_2SO_4 but not for HNO_3 and RCO_2H. The most effective oxidation reactions for dissolved SO_2 are (see review by Durham et al., 1982):

$$SO_{2(aq)} + H_2O \leftrightarrow H^+ + HSO_3^- \quad (16)$$

$$HSO_3^- + H_2O_{2(aq)} \rightarrow H^+ + SO_4^{2-} \quad \text{(unbalanced)} \quad (17)$$

$$HSO_3^- + O_{3(aq)} \rightarrow H^+ + SO_4^{2-} \quad \text{(unbalanced)} \quad (18)$$

The HSO_3^- - H_2O_2 reaction rate (Hoffmann and Jacob, 1984; Martin, 1984) is

$$-d[S(IV)]/dt = k_{19}\,[H_2O_2][H^+][HSO_3^-]\{0.1 + [H^+]\}^{-1} \quad (19a)$$

For unbuffered solutions, an important feature of the rate Eqn 19 is the catalytic influence of $[H^+]$ on the chemical rate. Formally, the product $[H^+][HSO_3^-]$ may be replaced with $K_{16}[SO_2 \cdot H_2O]$, where K_{16} is the dissociation constant. For $1.8 < pH < 6$, Eqn 19a becomes

$$-d[S(IV)]/dt = k_{19}\,[H_2O_2][SO_2 \cdot H_2O]\{0.1 + [H^+]\}^{-1} \quad (19b)$$

Thus, in an open system (such as atmospheric aerosol, cloud nuclei) in which the aqueous concentrations of $SO_2 \cdot H_2O$ and H_2O_2 are maintained through Henry's law, the oxidation proceeds independently of pH. That is, the increasing acidity of the particle does not slow the acidification rate for $pH > 1.8$. In the absence of mass transport limitations, the oxidation rate is

$$-d[S(IV)]/dt = 10k_{19}K_{16}H_{SO2}P_{SO2}H_{H2O2}P_{H2O2} \quad (20)$$

where P_i and H_i denote the gaseous partial pressure and Henry's law constant for species i.

The activation energy of Rxn 17 for unbuffered solutions has been estimated to be about 6.0 kcal/mole (Overton, 1985).

Several rate expressions for HSO_3^- - O_3 obtained over different pH (< 6.5) ranges applicable to atmospheric aerosol have been reported; the activation energy (6-8 kcal/mole) appears to be pH dependent (see Martin,

1984). For pH < 6.5, the various expressions reported have the following forms:

$$-d[S(IV)]/dt = k_{21}[H^+]^{-0.5}[O_3][S(IV)] \quad (21)$$

$$-d[S(IV)]/dt = K_{22a}[HSO_3^-](O_3] + k_{22b}[SO_3^{2-}]][O_3] \quad (22)$$

$$-d[S(IV)]/dt = k_{23a}[S(IV)][O_3] + k_{23b}[H^+]^{-1}[S(IV)][O_3] \quad (23)$$

In an open system in which the acidity of the aqueous particles increases, the oxidation (acidification) rates given by Eqns 21-23 decrease. For example, the oxidation rate for Rxn 22 without mass transport limitations is

$$-d[S(IV)] = K_{22a}K_{16}H_{SO2}P_{SO2}H_{O3}P_{O3}[H^+]^{-1} \quad (24)$$

Sensitivity analyses based on chemical reaction rates, Henry's law values, and ignoring selective mass transport resistances (see Martin, 1984) indicate that for $[H_2O_2]/[O_3] > 1/50$, the oxidation of dissolved SO_2 at pH < 5.6 is dominated by H_2O_2.

Substantial aqueous pathways for oxidizing NO_2 and NO have not been reported. Most likely, acidification of aerosol by oxidation of NO_2 and NO in atmospheric aqueous particles is not important, due to their low solubilities. Presently, the chemical sequence (Rxn 6) consisting of the formation, absorption, and hydration of N_2O_5 is regarded as the major pathway involving the aqueous phase (see Calvert and Stockwell, 1984; Chameides and Davis, 1982; Graedel and Weschler, 1981).

The organic chemistry of the aqueous phase is expected to be similar to the gas-phase photochemical cycle shown in Fig. 1. The role of the aqueous phase as reaction medium has been recognized for aerosols and cloud nuclei (Graedel and Weschler, 1981; Kuo, 1984) and for natural surface water systems (Zafiriou, 1983; Zepp, 1982; Zika 1981).

AQUEOUS-PHASE CHEMISTRY: CATALYZED

Transition metal ion catalytic oxidation of dissolved SO_2 by O_2 (see Martin, 1984; Hoffmann and Jacob, 1984) will not be reviewed here. The metal catalyzed rates do not appear to be competitive with those of the dissolved oxidants (Calvert, 1983), except perhaps near local sources that emit the metals in fine particles or as vapors.

Transition metal may play an important role in decomposing the dissolved oxidants to generate oxidizing free radicals (Hoffmann and Jacob, 1984). The evidence for O_3 catalyzed decomposition is conflicting (Martin, 1984; Hoffmann and Jacob, 1984). However, the catalyzed decomposition of H_2O_2 by transition metals produces HO and HO_2; the mixture, known as Fenton's Reagent," is commonly used to oxidize organic compounds (Czapski et al., 1971). The reaction scheme, using Fe^{3+} as an example, is

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^+ \quad (25)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO + OH^- \quad (26)$$

$$Fe^{2+} + HO \rightarrow Fe^{3+} + HO^- \quad (27)$$

$$HO + H_2O_2 \rightarrow H_2O + HO_2 \quad (28)$$

$$Fe^{2+} + HO_2 \rightarrow Fe^{3+} + HO_2^- \quad (29)$$

$$Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + HO_2 \quad (30)$$

$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + O_2 + H^+ \quad (31)$$

The oxidizing free radicals may attack the organic compounds (or other reductants) in the following manner:

$$HO + RH \rightarrow H_2O + R \quad (32)$$

$$R + O_2 \rightarrow ROO \quad (33)$$

$$R + Fe^{3+} \rightarrow Fe^{2+} + R^+ \quad (34)$$

$$ROO + Fe^{3+} \rightarrow R^+ + O_2 + Fe^{2+} \quad (35)$$

The organic free radical products R, R^+, and ROO enter into reactions that produce reactive aldehydes, ketones, alcohols, etc., which under continued attack by the oxidizing free radicals produce organic acids and carbon dioxide.

Metal ions having two valence states that are readily assessable in the atmosphere and that differ by one electron may form Fenton-like reagents with a similar scheme as shown above (Walling, 1975). Suitable metal-ion pairs likely to be found in fine aqueous particles include Fe^{3+}/Fe^{2+}, Cu^{2+}/Cu^{+}, Cr^{3+}/Cr^{2+}, and Mn^{3+}/Mn^{2+}. Mixtures of these metal ions (e.g., Fe and Cu ions) and with others that include valence states differing by two electrons (Zn, Cd) produce synergistic catalysis of the decomposition of H_2O_2 (Baxendale, 1952).

The Fenton reaction may be important to generating oxidizing free radicals not only in atmospheric aqueous particles, but also in aqueous films on surfaces and in surface waters. Reductants present in the film or surface will be oxidized, with the likely end-products being mineral or organic acid (or CO_2).

CONCLUSIONS

This review has presented evidence that the photochemical oxidation cycle, which produces the molecular oxidants H_2O_2 and O_3, participates indirectly in the acidification of atmospheric aqueous particles and surface films. These oxidants either react directly with the dissolved reductants (or ionic forms), or they are catalytically decomposed in processes that yield oxidizing free radicals.

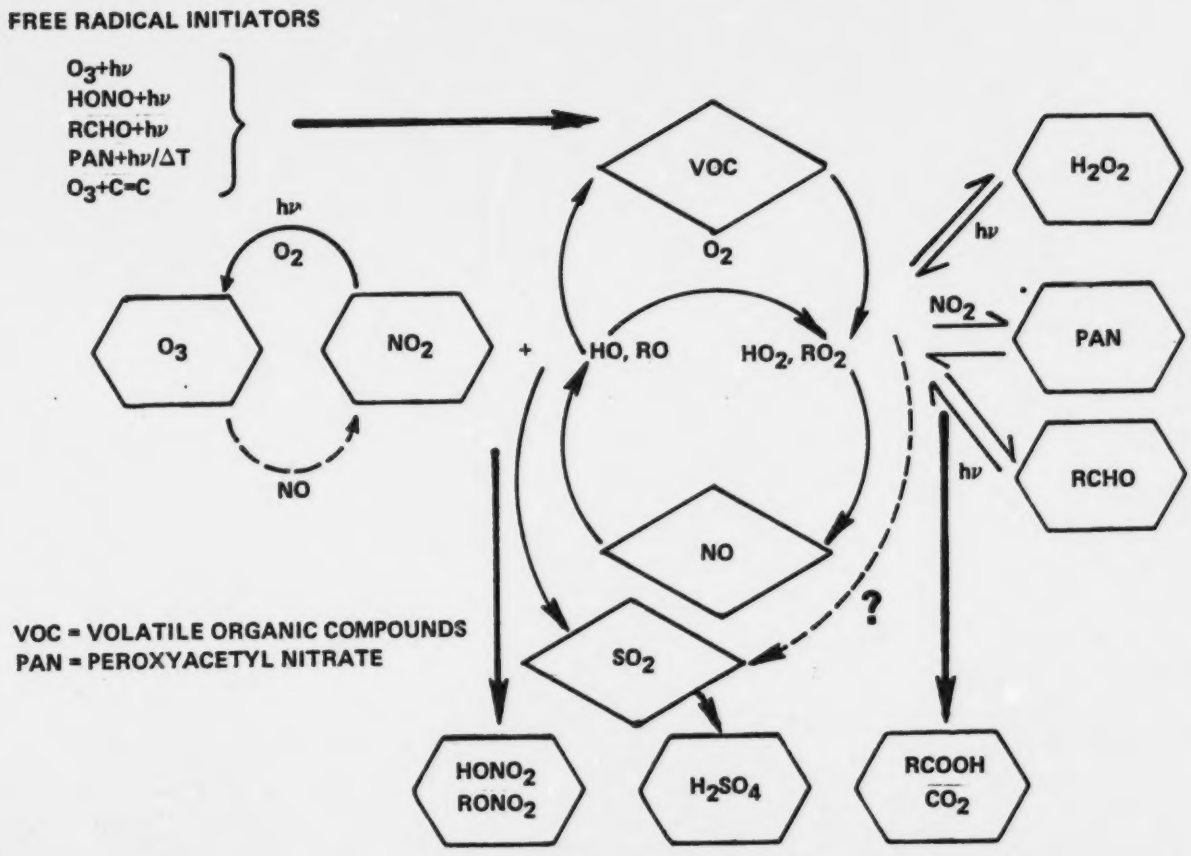

Figure 1. Schematic of the polluted atmospheric photo-oxidation cycle. Pollutants emitted from anthropogenic sources are shown in diamond boxes; pollutants formed in the atmosphere are shown in hexagonal boxes.

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